



**Corso di Dispositivi Elettronici - A. A. 2004/2005**

## **Semiconductor Materials**

## Semiconductor Structures and Parameters

- Important semiconductors
- Crystal structures
- Physical properties
- Brillouin zone
- Band structure
- Effective mass
- Doping
- Carrier concentration
- Electrical conductivity

- Important semiconductors

**Group IV materials**

- elements: C (diamond), Si, Ge
- compound: SiC
- solid solution:  $\text{Si}_x\text{Ge}_{1-x}$ ,  $x = 0 \dots 1$

**III-V compounds**

- GaAs, AlAs, InP, ...
- low gap: InAs, InSb
- wide gap: GaN, AlN
- solid solutions:  $\text{Ga}_x\text{Al}_{1-x}\text{As}$ , ...

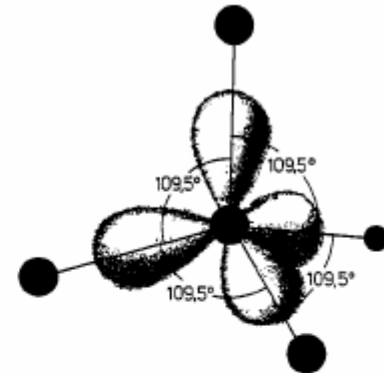
**II-VI compounds**

- ZnSe, CdTe
- wide gap: ZnS, MgS
- solid solutions:  $\text{Zn}_x\text{Mg}_{1-x}\text{S}_y\text{Se}_{1-y}$ , ...

- Crystal structures

### Coordination

- fourfold (tetrahedral) coordination
- directed bonding: tetraeder
- 4 bonds x 2 electrons = 8 electrons



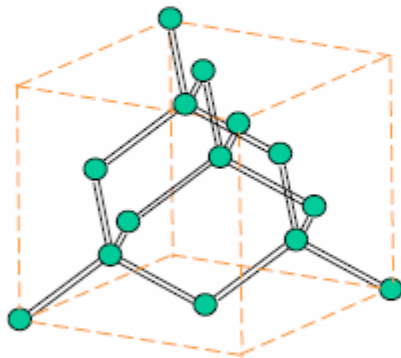
### Bonding

- covalent: group IV elements C, Si, Ge
- Mixed covalent – ionic: compounds SiC, GaAs, ...
- Ionic character depends on electronegativity  $\chi$   
 $\chi(\text{Ga}) = 1.81$  ,  $\chi(\text{As}) = 2.18$

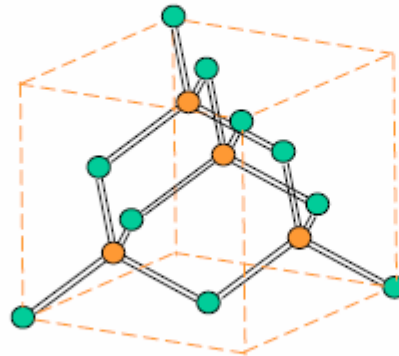
- Crystal structures

### Face centred cubic (zinkblende)

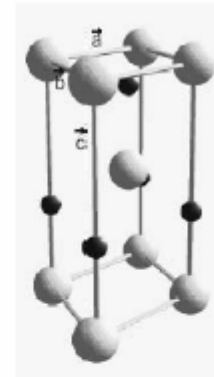
C, Si, Ge



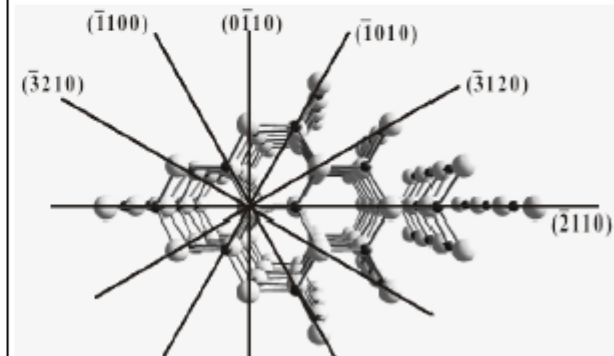
GaAs, ZnS,  
 $\beta$ - or 3C SiC,  
cubic GaN



### Hexagonal (wurtzit)



GaN,  
AlN, 2H  
SiC

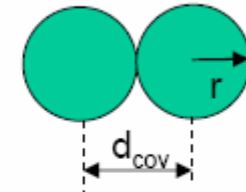


<http://www.ub.uni-konstanz.de>

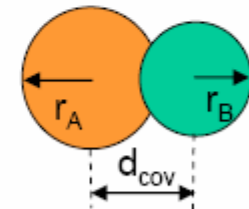
- Physical properties

### Covalent bond length $d_{\text{cov}}$

- Group IV elements: C, Si, Ge:  $d_{\text{cov}} = 2 \cdot r$ 
  - $r$  covalent radius



- Compounds:  $d_{\text{cov}} = r_A + r_B - c|\chi_A - \chi_B|$ ;  $c = 0.02 \dots 0.08 \text{ \AA}$ 
  - $\chi$  - electronegativity of atoms
  - electron charge transfer  $\Delta q = |\chi_A - \chi_B|$
  - electrical dipole moment  $p = \Delta q \cdot e \cdot d_{\text{cov}}$



- Physical properties

Covalent radii  $r$  (Å) and electronegativity  $\chi$  after Pauling

	II	III	IV	V	VI
$\chi$ →	1.57	2.04	1.55	3.04	3.44
	Be	B	C	N	O
$r$ →	1.06	0.88	0.77	0.70	0.73
	1.31	1.61	1.90	2.19	2.58
	Mg	Al	Si	P	S
	1.40	1.26	1.17	1.10	1.04
	1.65	1.81	2.01	2.18	2.55
	Zn	Ga	Ge	As	Se
	1.31	1.26	1.22	1.18	1.14
		1.78		2.05	2.10
		In		Sb	Te
		1.44		1.36	1.32

- Physical properties

If the covalent bond length  $d_{\text{cov}}$  increases  $\uparrow$ , then..

Mechanical properties

- Elastic constants  $\downarrow$
- Thermal conductivity  $\downarrow$

Optical properties

- Refractive index, dielectric constant  $\uparrow$

Electronic properties

- Band gap  $\downarrow$
- Effective mass  $\downarrow$
- Carrier mobility  $\uparrow$
- Ionization energy  $\downarrow$
- Breakdown field  $\downarrow$

$\Rightarrow$  High power, high temperature electronics:  $d_{\text{cov}} \downarrow$

$\Rightarrow$  High frequency, low power electronics:  $d_{\text{cov}} \uparrow$



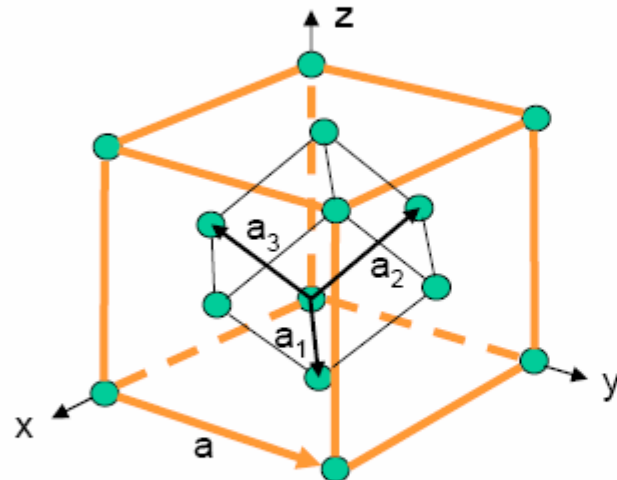
- Brillouin zone

## The reciprocal space

- Real space

Atomic position:  $R = m_1 a_1 + m_2 a_2 + m_3 a_3$ 

Face centred cubic (fcc) lattice: Si



$$a_1 = a/2 (i + j)$$

$$a_2 = a/2 (j + k)$$

$$a_3 = a/2 (i + k)$$

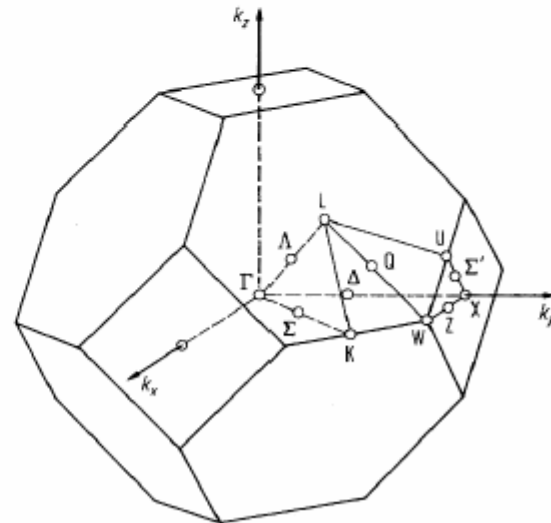
- Reciprocal space

Reciprocal space vector  $G = hg_1 + kg_2 + lg_3$ 

$$g_i \cdot a_j = 2\pi \delta_{ij} \Rightarrow \exp(iR \cdot G) = 1$$

$$g_i = 2\pi \frac{a_i \times a_j}{a_i(a_j \times a_k)} \quad i, j, k : \text{cycl.}$$

bcc – body centred cubic



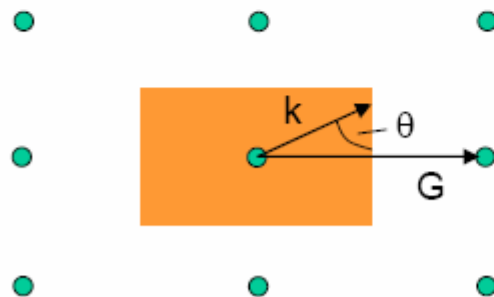
- Brillouin zone

Smallest polyhedron confined by planes perpendicular bisecting the reciprocal lattice vector.

One dimension



Two dimensions



Three dimensions

$$\mathbf{g} \cdot \mathbf{G} = \frac{G^2}{2} \quad k = \frac{2\pi}{\lambda}$$

$2 \cdot \mathbf{k} \cdot \mathbf{G} = G^2$  condition for Bragg reflection of traveling electrons

$$d(h,k,l) = 2\pi/G \rightarrow 2d \cdot \sin\theta = \lambda$$

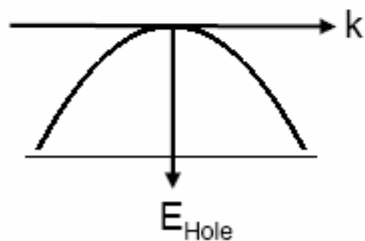
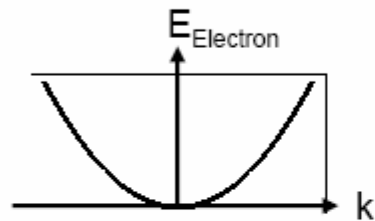
- Band structure

## Electrons in a periodic potential

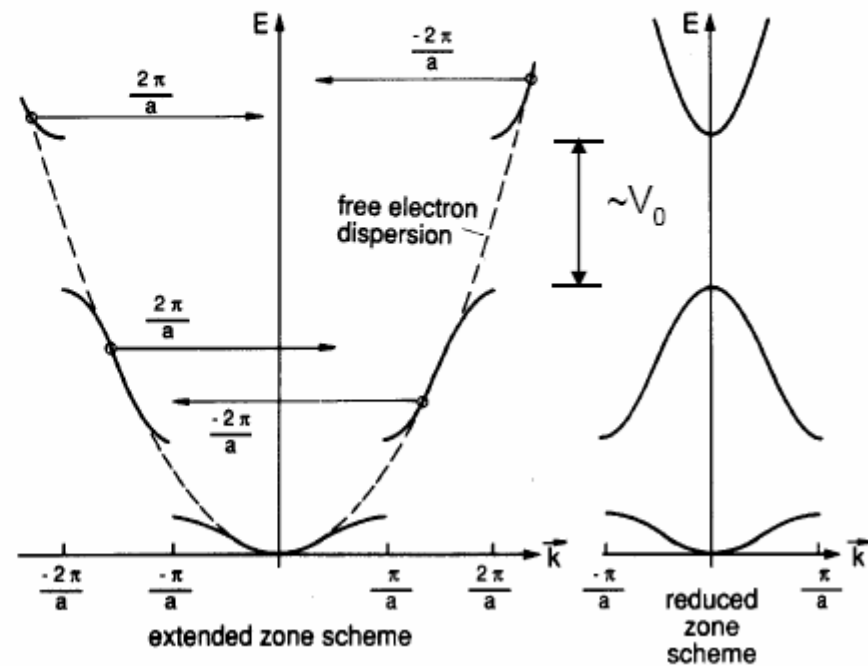
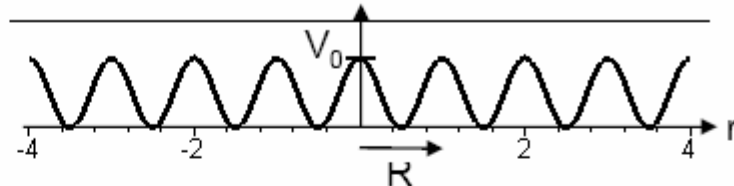
- Free electron ( $V=0$ )

$$E = E_{\text{kin}} = \frac{p^2}{2 \cdot m_e} = \frac{\hbar^2}{2 \cdot m_e} k^2$$

curvature

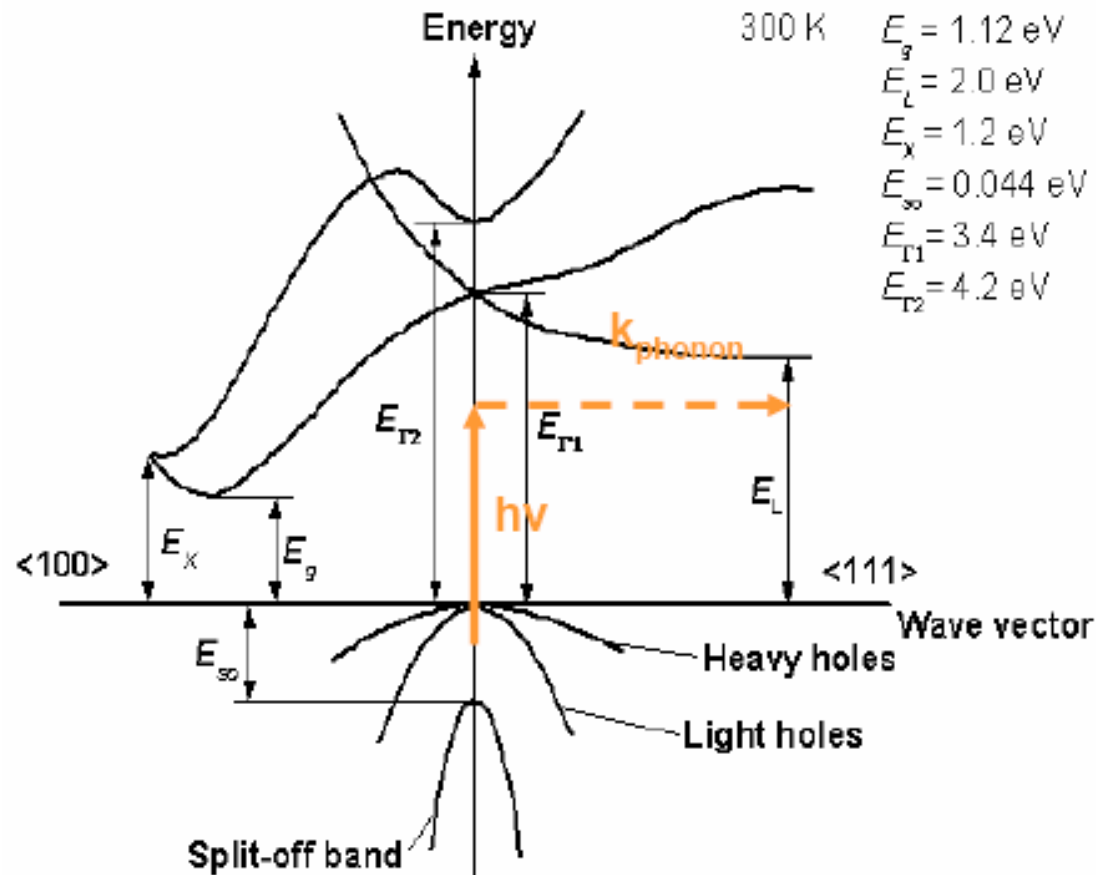


- Periodic potential  $V(r) = V(R+r)$



- Band structure

## Indirect semiconductor



- Band structure

## Indirect semiconductor

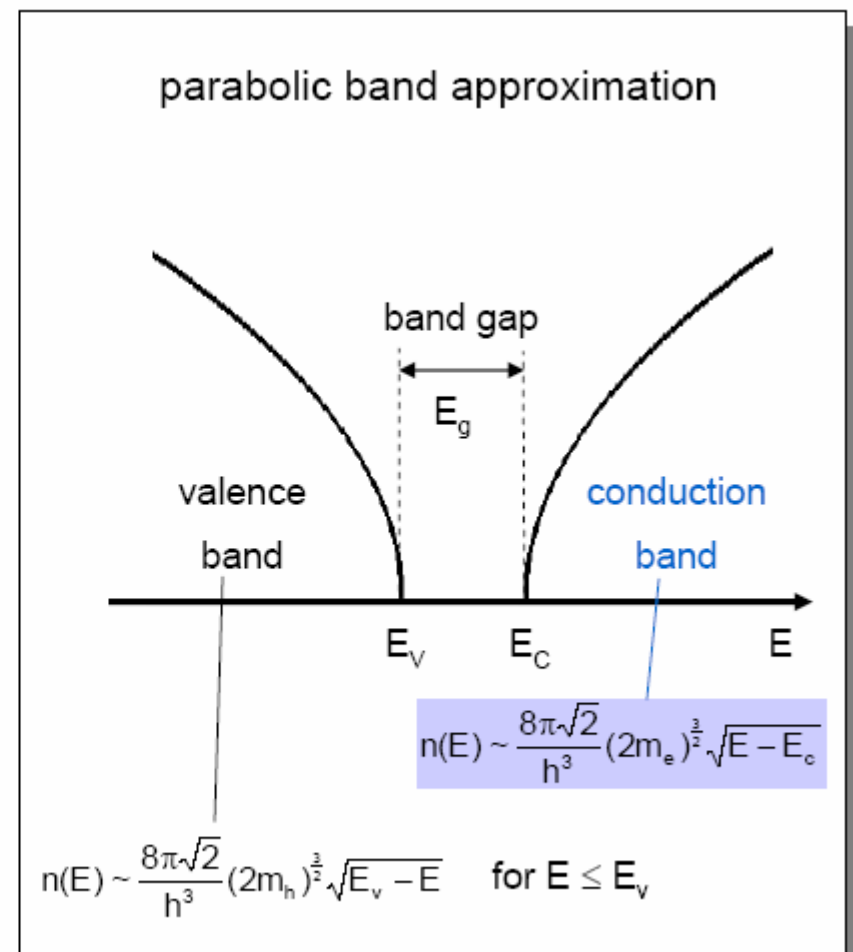
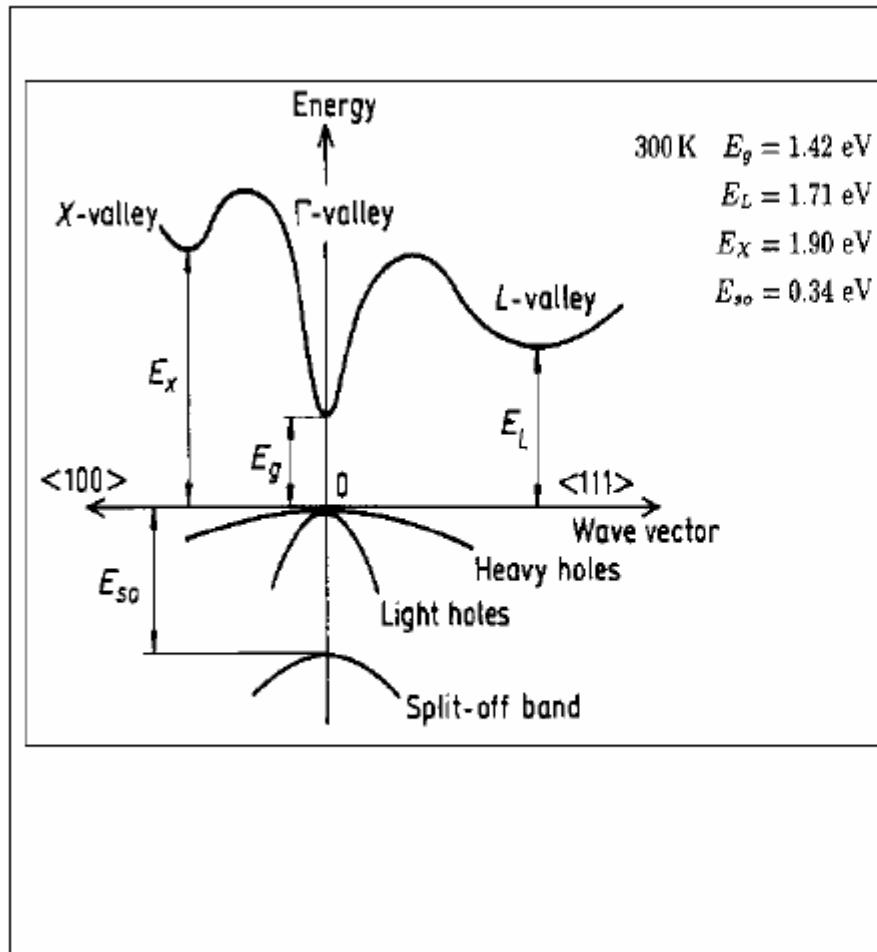
## Optical transition: absorption or emission of a photon

- $E_{\text{Photon}} = h \cdot \nu = \Delta E_{\text{Electron}}$
- $p_{\text{Photon}} + p_{\text{Phonon}} = \underbrace{h/\lambda_{\text{Photon}} + h/\lambda_{\text{Phonon}}}_{\approx 0, \text{ because } \lambda_{\text{Photon}} \gg \lambda_{\text{Phonon}}} = \Delta p_{\text{Electron}}$

consequence: low probability

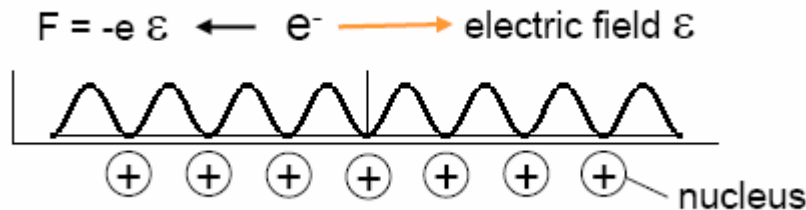
- Band structure

## Direct semiconductor



- Effective mass

### The acceleration theorem in the reciprocal space



$$\text{Force } F = \frac{dp}{dt} = \hbar \frac{dk}{dt} = -e E$$

$$\text{Energy } E(k) = \frac{p^2}{2 \cdot m_e} = \frac{\hbar^2 k^2}{2 \cdot m_e} \quad \longrightarrow \quad \frac{dE}{dk} = \nabla_k E(k) = \frac{\hbar^2 k}{m_e} = \frac{\hbar}{m_e} p = \hbar v \quad \text{velocity}$$

The electron velocity  $v$  is proportional to the band inclination.

$$\text{acceleration } \frac{dv_i}{dt} = \frac{1}{\hbar} \frac{d}{dt} (\nabla_k E)_i = \frac{1}{\hbar} \sum_{j=1}^3 \frac{\partial^2 E}{\partial k_i \partial k_j} \frac{dk_j}{dt} = \frac{F_j}{m_e} \quad \text{with} \quad \frac{1}{m_e} = \frac{1}{\hbar^2} \sum_{j=1}^3 \frac{\partial^2 E}{\partial k_i \partial k_j}$$

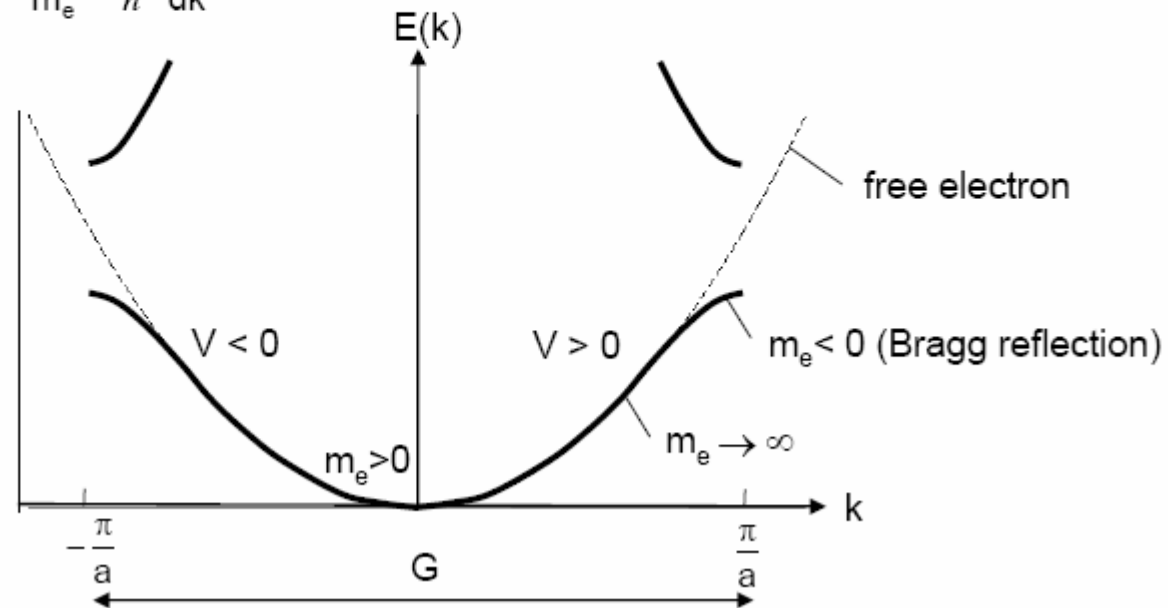
The electron effective mass tensor  $m_e$  is reciprocal to the band bend.

- Effective mass

Momentum formula  $F = m \cdot \frac{dv}{dt}$

Relation between electron velocity  $v$  and crystal momentum  $p = \hbar k$ :  $v = \frac{\hbar k}{m_e}$

One dimension:  $\frac{1}{m_e} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2}$



Acceleration theorem in the reciprocal space:

The response to an external force is equal to the derivative of the crystal momentum and not to the derivative of the electron momentum.



- Doping

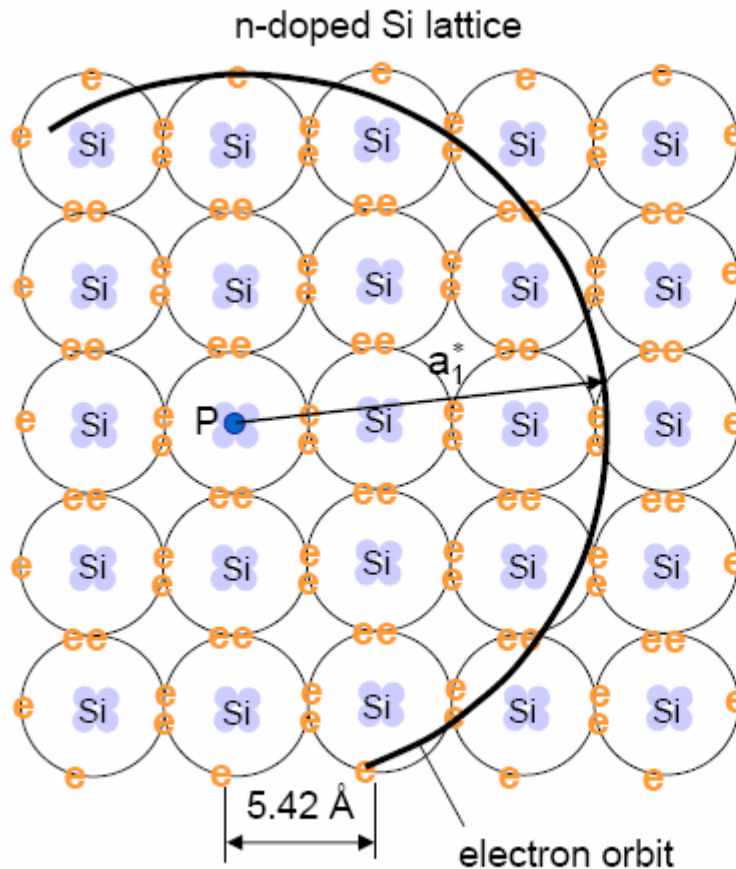
Main difference between semiconductor and insulator: a semiconductor can be doped.

Semiconductor	p - dopant	n - dopant
Si SiC	group III: Al, Ga Al	group V: N, P N
GaAs GaN	group II: Be, Zn Mg	group IV: C, Si Si
ZnSe	group V: N	group VII: Cl

Site-competition epitaxy: Si/C  $\uparrow$ : N concentration  $\uparrow$  (N replaces C)

Si/C  $\downarrow$ : Al concentration  $\uparrow$  (Al replaces Si)

- Doping

Ionization energy  $E_i$  of dopants

Energy eigenvalues  $E_n$  of a pseudo-hydrogen atom

$$E_n = - \underbrace{\frac{m_0 \cdot e^4}{2(4\pi\epsilon_0)^2 \hbar^2}}_{13.6 \text{ eV}} \cdot \frac{1}{n^2} \cdot \frac{m_e}{m_0 \cdot \epsilon^2}$$

$m_0$  - electron mass

$m_e$  - effective electron mass

$\epsilon$  - dielectric constant

Bohr's radius  $a_1$  of the electron orbit

$$a_1^* = \epsilon \cdot \frac{m_0}{m_e} \cdot a_1 \quad \text{with } a_1 = 0.53 \text{ Å}$$

- Doping

### Ionization energy $E_i$ of n-dopants

Material	$a_{\text{cubic}}$ (Å)	$E_g$ (eV)	$m_e/m_0$	dielectric constant $\epsilon$	$E_i$ (meV)		$e^{-\frac{E_i}{kT}}$ T = 300 K
					measured	$13.6\text{eV} \frac{m_e}{m_0 \epsilon^2}$	
InAs	6.06	0.35	0.023	14.6	1	1.5	0.96
Ge	5.66	0.66	0.12	16.2	13	6.7	0.60
Si	5.43	1.12	0.26	11.9	45	25	0.17
GaAs	5.65	1.42	0.067	10.9	6	7.2	0.79
4H-SiC		3.23	0.29	9.72	66	42	0.08
GaN		3.51	0.21	10.0	20	28	0.92
C	3.57	5.47	0.48	5.7	~ 1000	200	$< 10^{-5}$

Room temperature kinetic energy  $kT = 25.8$  meV

Strong atomic bond causes high ionization energy of dopants.

- Carrier concentration

## Undoped (intrinsic) semiconductor

Fermi statistics  $f(E) = \frac{1}{1 + e^{\frac{E-E_F}{kT}}} \sim e^{-\frac{E-E_F}{kT}}$  Boltzmann statistics

$E-E_F \gg kT$

Intrinsic carrier concentration  $n_i$ 

Law of mass action

$$n_i^2 = n \cdot p = N_C \cdot N_V e^{-\frac{E_g}{kT}}$$

Si (300 K):  $n_i = p_i = 10^{10} / \text{cm}^3$ Density of Si atoms:  $5 \cdot 10^{22} / \text{cm}^3$ 

$$N_C = 2 \left( \frac{2\pi m_e kT}{h^2} \right)^{\frac{3}{2}} \quad N_V = 2 \left( \frac{2\pi m_h kT}{h^2} \right)^{\frac{3}{2}}$$

Position of the Fermi level (chemical potential):  $E_F = E_C - \frac{E_g}{2} + \frac{3}{4} kT \ln \frac{m_h}{m_e}$

- Carrier concentration

n-doped, doping concentration  $N_d$

electron concentration:  $n_0 = \frac{\sqrt{N_d^2 + 4n_i^2} + N_d}{2} \approx N_d$

hole concentration:  $p_0 = \frac{\sqrt{N_d^2 + 4n_i^2} - N_d}{2} \approx \frac{n_i^2}{N_d}$   $E_d < kT$

p-doped, doping concentration  $N_a$

hole concentration:  $p_0 = \frac{\sqrt{N_a^2 + 4n_i^2} + N_a}{2} \approx N_a$

electron concentration:  $n_0 = \frac{\sqrt{N_a^2 + 4n_i^2} - N_a}{2} \approx \frac{n_i^2}{N_a}$   $E_a < kT$

- Carrier concentration

Intentionally doped semiconductor: dopant distance

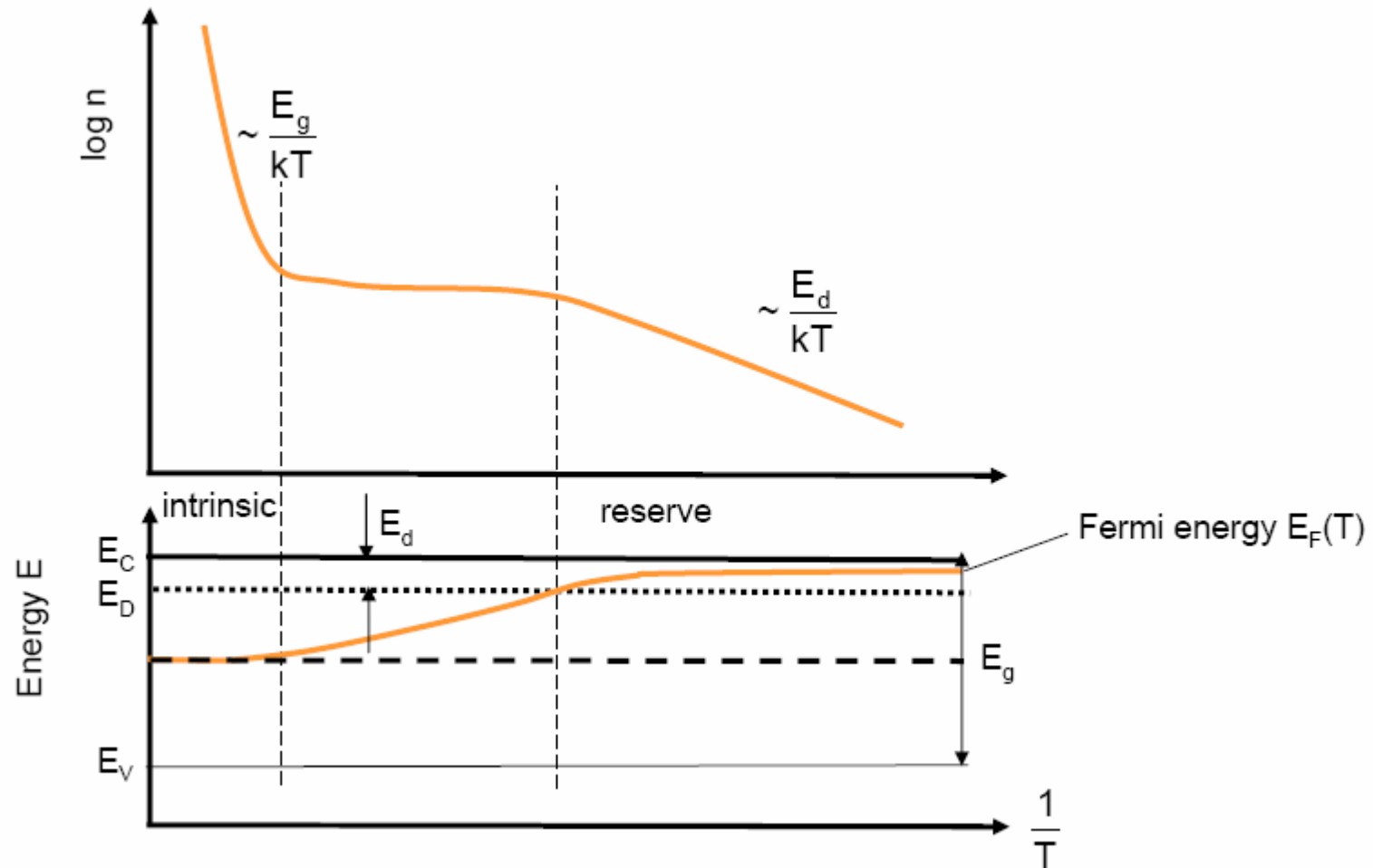
Doping concentration	Relative carrier concentration	Mean Distance between dopants
$10^{14} \text{ cm}^{-3}$	$2 \cdot 10^{-9}$	794 atoms
$10^{17} \text{ cm}^{-3}$	$2 \cdot 10^{-6}$	79 atoms
$5 \cdot 10^{19} \text{ cm}^{-3}$	$1 \cdot 10^{-3}$	10 atoms

Degenerate semiconductor → overlap of the wave functions  
→ temperature independent conductivity  
→ Ohmic contact

Density of Si atoms:  $5 \cdot 10^{22} / \text{cm}^3$

- Carrier concentration

## Temperature dependence



- Electrical conductivity

Two parts in electrical current:

- Electrical field (potential gradient) related:  $j_1 = e\mu n\mathcal{E}$
- Concentration gradient related:  $j_2 = eD \frac{dn}{dx}$

Total current density:

- electrons:  $j_e = e\mu_e n\mathcal{E} + eD_e \frac{dn}{dx}$
- holes:  $j_h = e\mu_h n\mathcal{E} + eD_h \frac{dp}{dx}$



## ■ Electrical conductivity

There is no resistance for free carriers in a periodic potential, but:

any disruption produces collisions with characteristic times  $\tau_1, \tau_2, \tau_3, \dots$

- Temperature dependent phonon scattering  $\tau_p \sim T^{-3/2}$
- Collisions with ionized impurities  $\tau_i \sim T^{3/2}$
- Collisions with optical phonons in polar semiconductors
- Intervalley scattering

Addition of the probabilities for collisions  $\frac{1}{\tau} = \frac{1}{\tau_p} + \frac{1}{\tau_i} + \dots$

Carrier mobility:  $\mu_e = \frac{e\tau_e}{m_e}$  ;  $\mu_h = \frac{e\tau_h}{m_h}$

Electrical conductivity  $\sigma = e(n\mu_e + p\mu_h) = \sigma_e + \sigma_h$

Electrical current density  $j = j_e + j_h = \sigma \mathcal{E}$

Einstein relation for the diffusion coefficient  $D = \frac{kT}{e}\mu$  in  $j = -D \frac{\partial n}{\partial x}$

- Electrical conductivity

## Improvements

### The carrier mobility limits the device speed

**Problem:** No carriers without doping, but ionized carriers cause collisions:  $\mu \downarrow$

**Solution:** Heterostructures

### How to increase the mobility in Si?

**Decrease the intervalley scattering** → strained Si

Cubic symmetry → 3-fold degenerate band structure

Biaxial strain → rhombohedral symmetry → split-off band structure

$\mu_h$  enhancement ~ 2.5

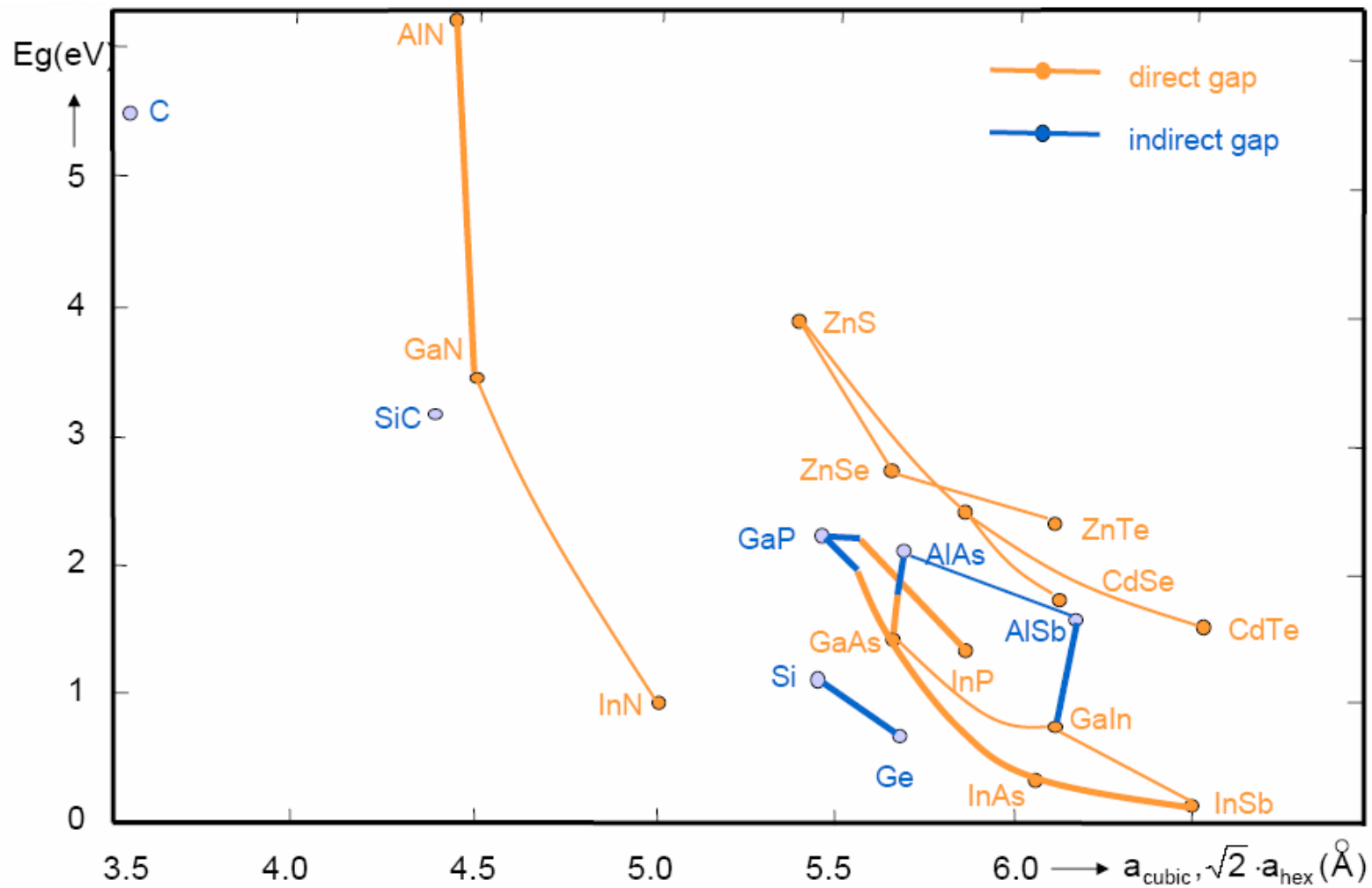
$\mu_e$  enhancement ~ 1.7

Best solution: uniaxial strain in the current direction (channel)

## Heterostructures

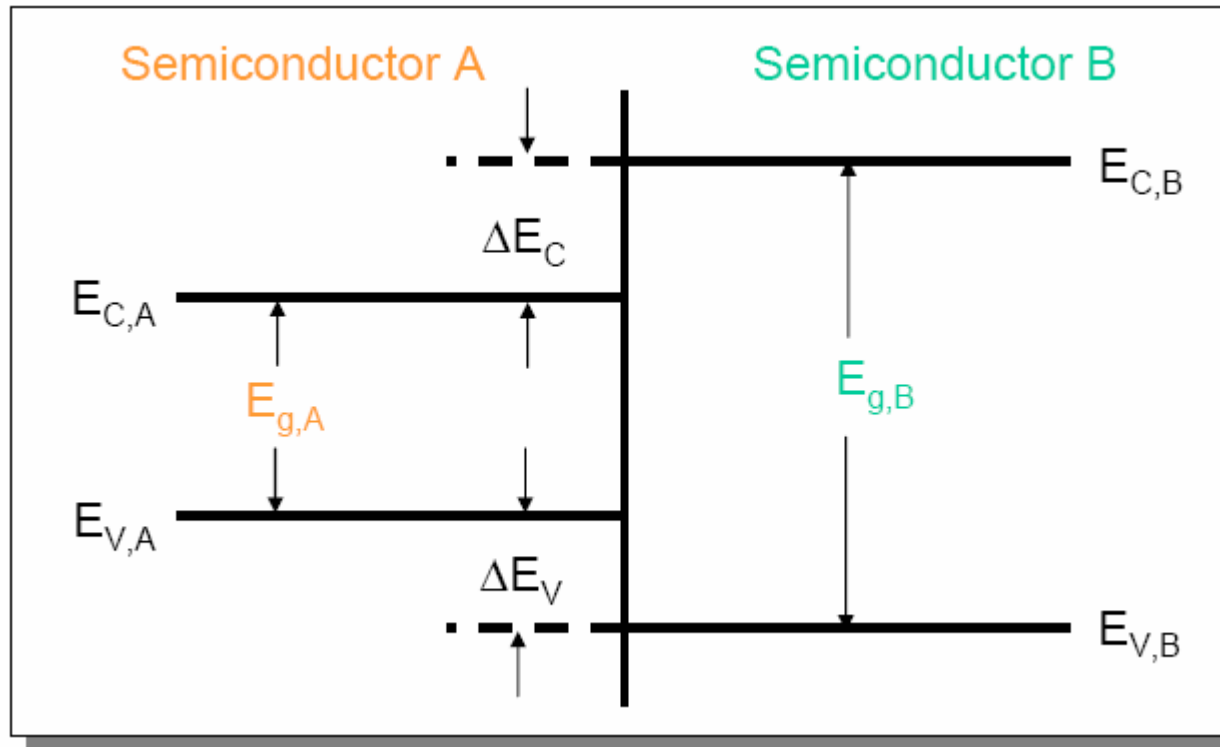
- Heterostructure
- Semiconductor alloys
- Heteroepitaxy
- Size quantization
- Carrier transport
- Spontaneous polarization

## Heterostructures



- Heterostructure

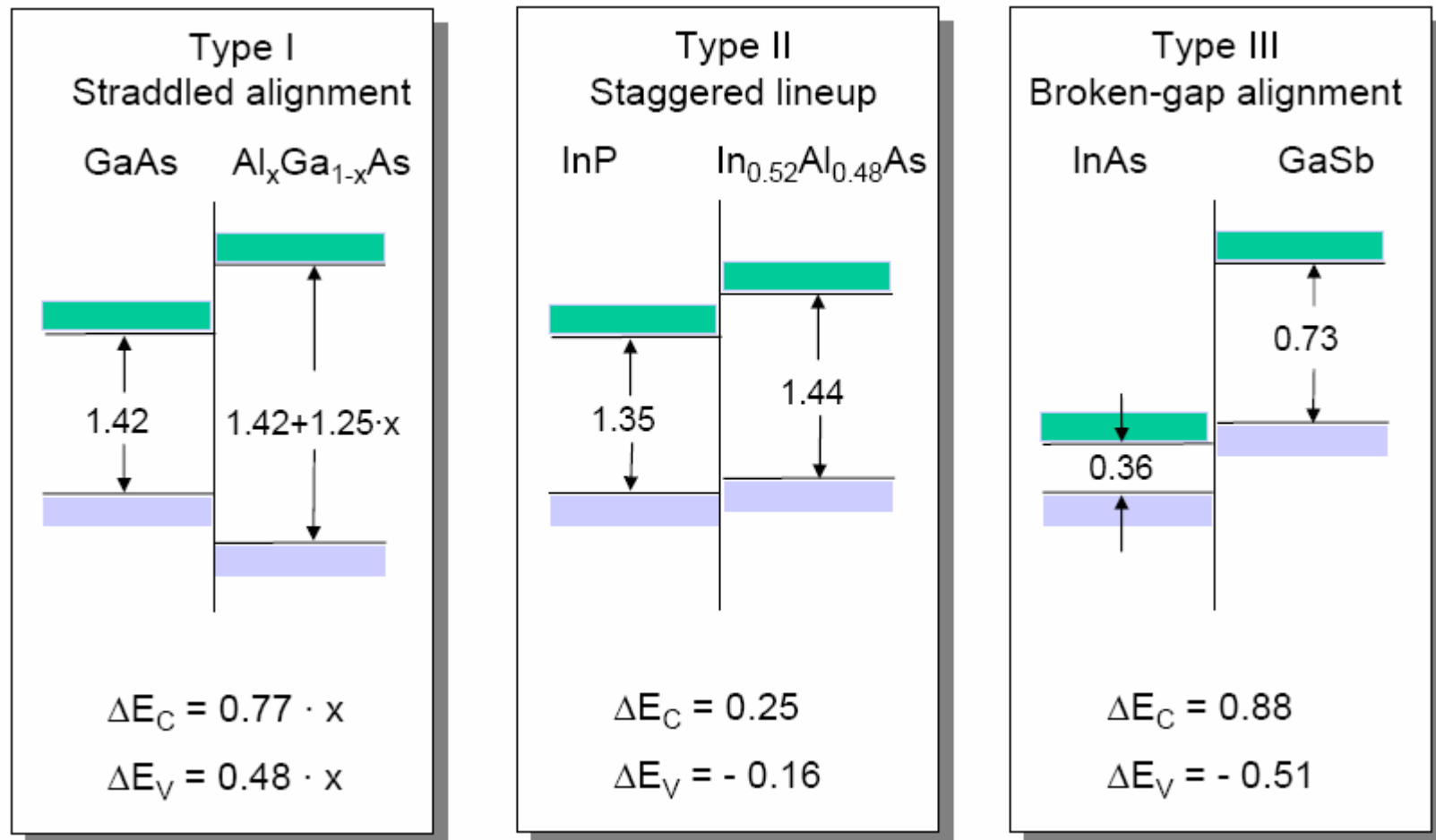
Definition of the band edge discontinuity  $\Delta E$



$$E_{g,B} - E_{g,A} = \Delta E_V + \Delta E_C$$

- Heterostructure

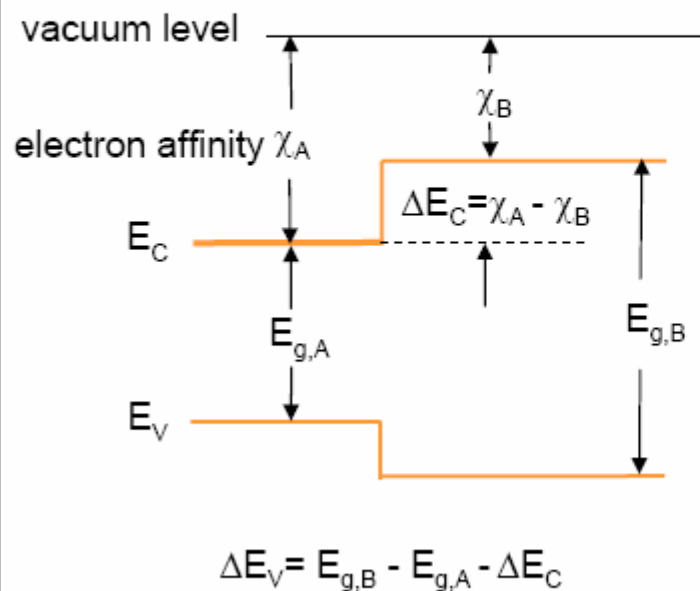
### Heterojunction band alignment (energy in eV)



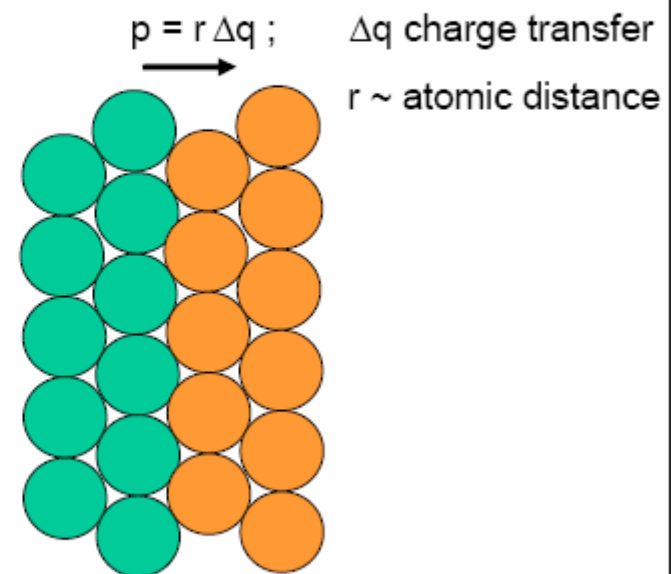
- Heterostructure

### Physical explanations for band lineups

#### Electron affinity rule for van der Waals epitaxy heterointerfaces



#### Interface dipol $p$ for interfaces between polar materials



## ■ Semiconductor alloys

### Band engineering: gap energy

„A“ and „B“ are chemically miscible semiconductors

→ mixed compounds, called **semiconductor alloy**  $A_xB_{1-x}$

x: mole fraction of A in the compound

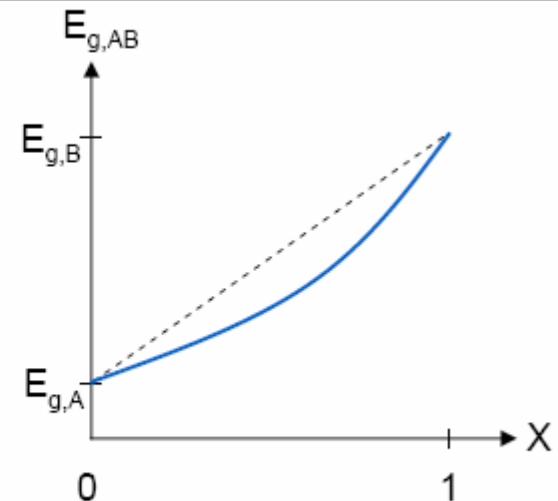
**Gap energy**  $E_{g,AB}$  of the alloy  $A_xB_{1-x}$ :

$$E_{g,AB} = \underbrace{x \cdot E_{g,A} + (1-x) \cdot E_{g,B}}_{\text{linear term}} + \underbrace{x \cdot (1-x) \cdot E_b}_{\text{Bowing parameter}}$$

for  $(AlAs)_x (GaAs)_{1-x}$  the bowing parameter is vanishingly small

Reason for bowing:

- different covalent radii
- different electronegativity





- Semiconductor alloys

Common anion rule

In compound semiconductor heterostructures with a common anion element (AlGaAs/GaAs) the valence band offset is smaller than the conduction band offset.

$$\text{InAs/GaAs:} \quad \frac{\Delta E_c}{\Delta E_v} \cong \frac{5}{1}$$

$$\text{GaAs/AlGaAs:} \quad \frac{\Delta E_c}{\Delta E_v} \cong \frac{3}{2}$$

- Semiconductor alloys

Lattice constant  $a$

Vegards rule for the lattice constant:  $a_{AB} = a_A x + a_B (1-x)$

Heterojunction lattice misfit:  $f = \frac{a_A - a_B}{a_A}$

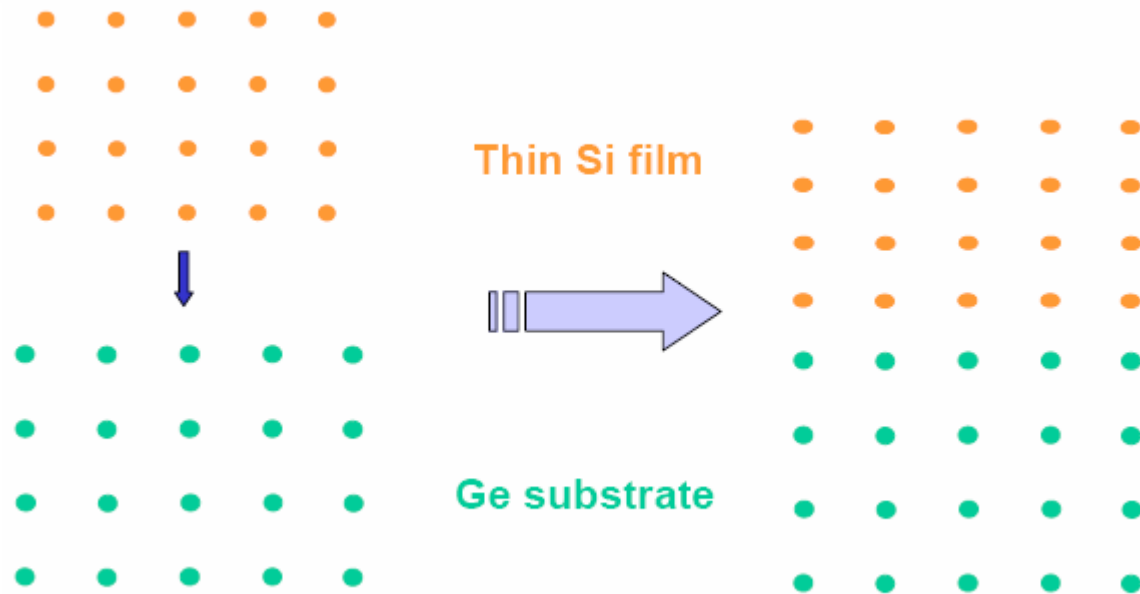
Types of heteroepitaxy:

- pseudomorphic growth
- growth with misfit dislocations
- metamorphic growth

- Heteroepitaxy

Pseudomorphic growth

Growth of materials with small lattice misfit without defects



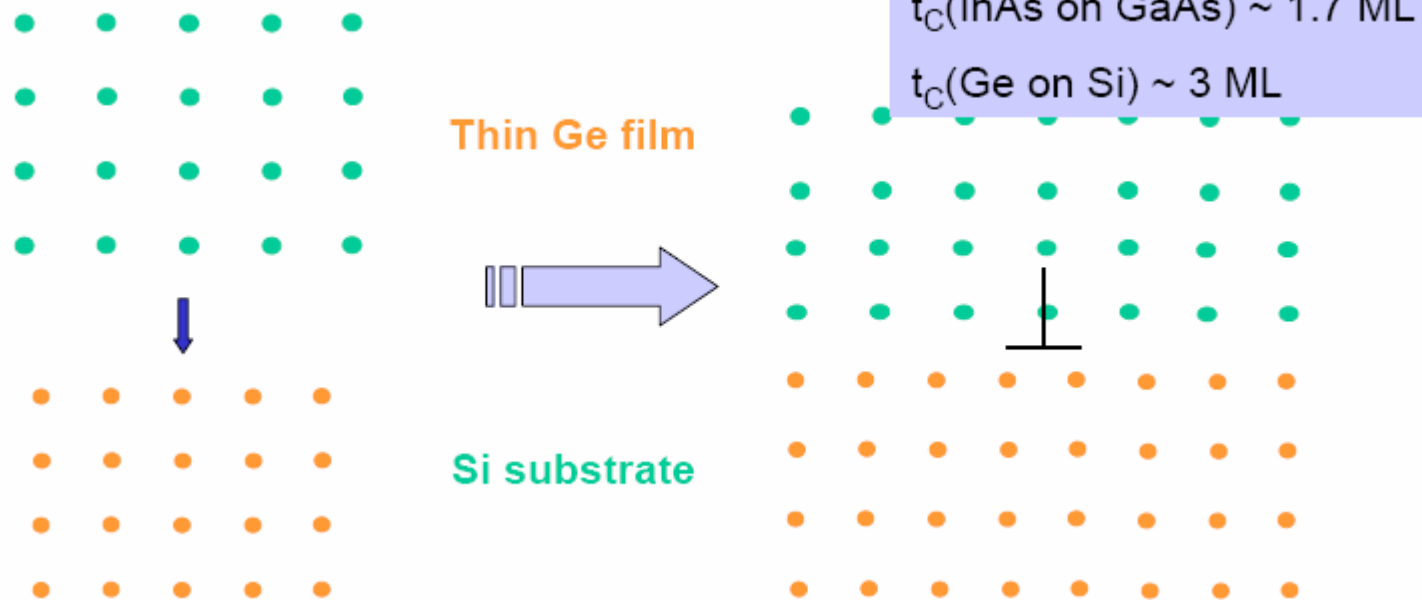
Result: Si film with two-dimensional mechanical stress

- Heteroepitaxy

Relaxed heterostructure growth

Above critical thickness  $t_c$ : relaxation by misfit dislocations,

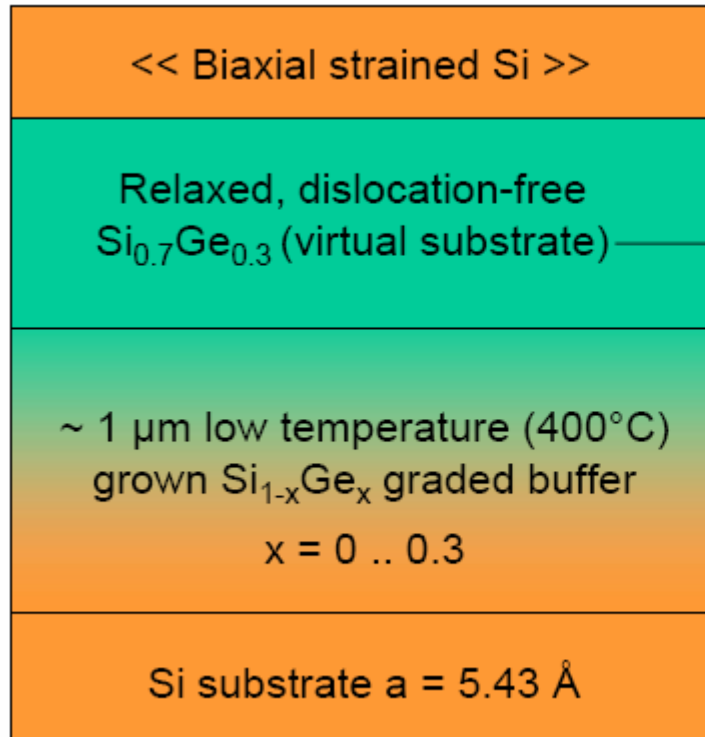
$$t_c \sim \frac{1}{f}$$



Result: Ge film with threading dislocations

## ■ Heteroepitaxy

### Metamorphic growth



#### Aim of a virtual substrate:

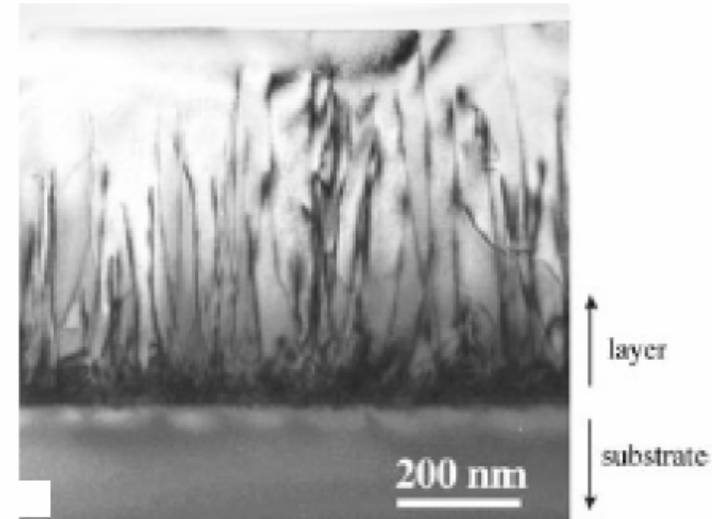
- Virtual substrate with lattice constant different from the real substrate for strained Si or SiGe HBT
- Dislocation-free, fully relaxed top layer with the same lattice constant in-plane and vertical

Metamorphic substrate = dislocation-free, different lattice substrate

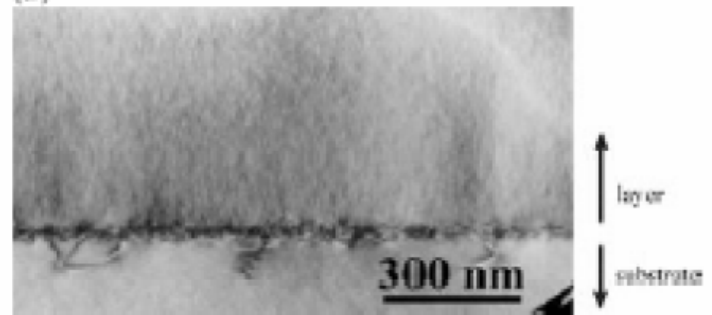
- Heteroepitaxy

Metamorphic growth

Relaxed heterostructure growth  
with threading dislocations



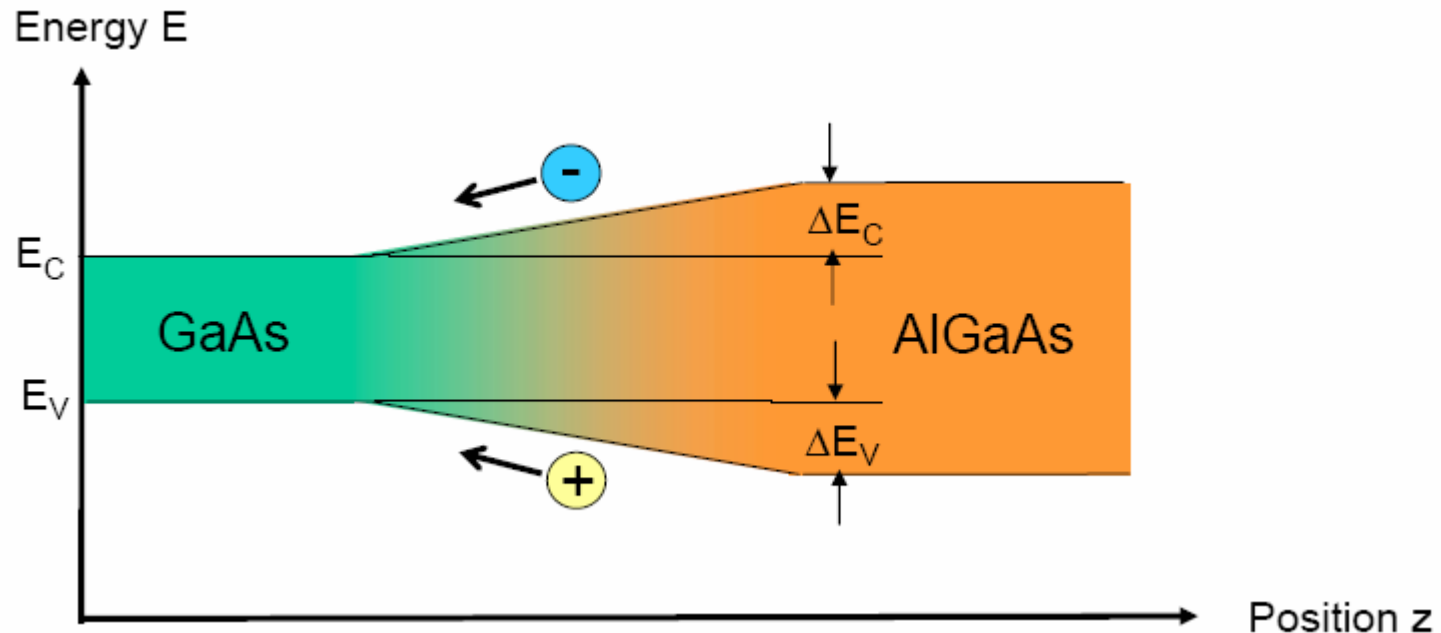
Metamorphic growth on low  
temperature grown buffer



Nanotechnology **15** (2004) S283–S287

- Heteroepitaxy

Linear graded composition



The graded region creates a quasi-electric field

- Size quantization

Structures with restricted freedom of motion for carriers due to potential barriers in heterostructures:

- 2D: two dimensional electron gas (2 DEG) confined in a quantum well



- 1D: motion of carriers only along one direction „Quantum Wire“



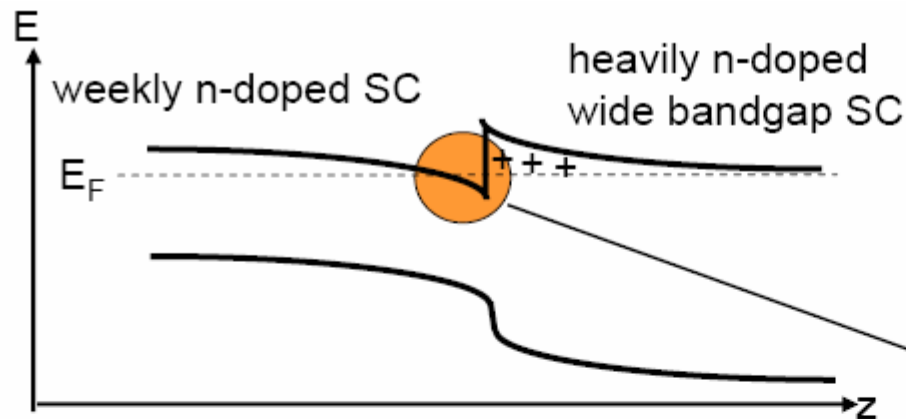
- 0D: confinement of carriers in a box „Quantum Dot“





- Size quantization

## Single heterostructure

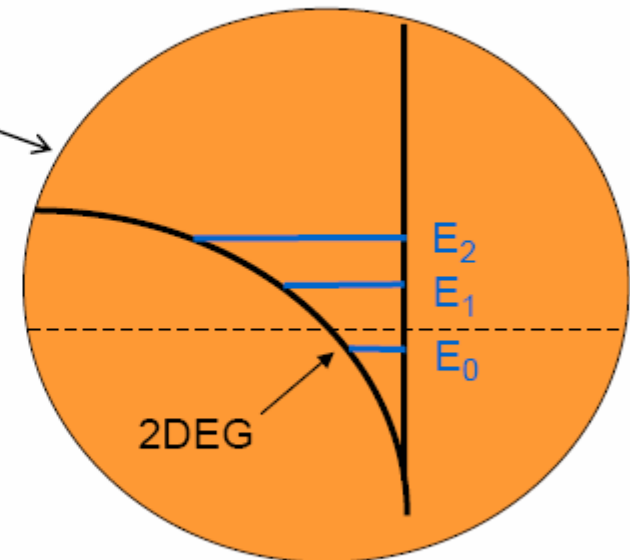


z-component of the Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2m_{e,z}} \frac{\partial^2}{\partial z^2} - eV(z) \right] \phi_i(z) = E_i \phi_i(z)$$

Energy eigenvalues:

$$E_i = \left( \frac{\hbar^2}{2m_{e,z}} \right)^{1/3} \left( \frac{3}{2} \pi e \varepsilon \right)^{2/3} \left( i + \frac{3}{4} \right)^{2/3}$$

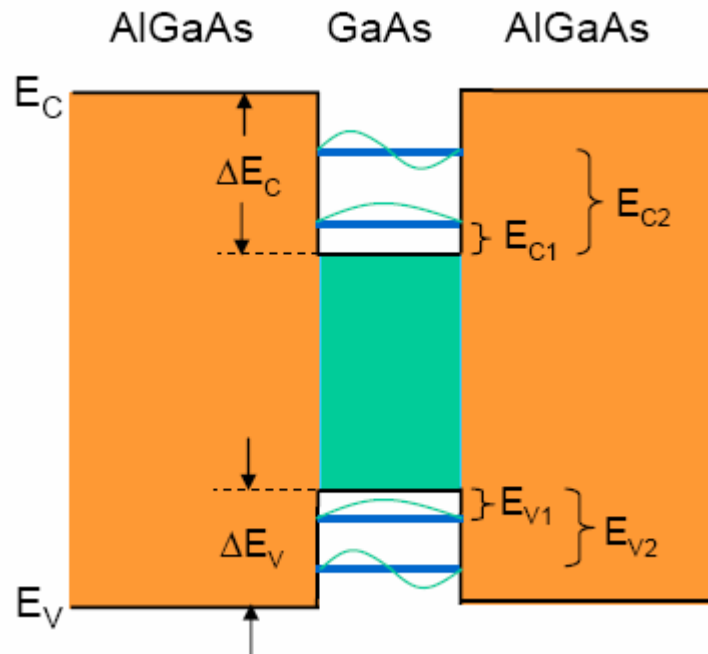


e - electronic charge

$\varepsilon$  - electric field

- Size quantization

### Double heterostructure: quantum well (QW)



Quantization of the momentum  $p_z$ :

$$p_z = \frac{\hbar}{\lambda_z} = i \frac{h}{2d} \quad \left( d = i \frac{\lambda}{2} \right)$$

Energy eigenvalues for  $E_{Ci} \ll \Delta E_C$ :

$$E_{Ci} = \frac{p_z^2}{2m_e} = \frac{h^2}{8m_e d^2} i^2$$

Electrons (holes) move in the x-y plane:

$$E_C(\vec{k}) = E_{Ci} + \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2)$$

Main effects: - in electronics high carrier mobility in undoped QW  
 - in optoelectronics reduced density of states

- Size quantization

### Quantum well conditions

Size quantization takes place if:

- the well width  $d_z < \text{mean free path between scatter}$
- $d_z < \text{De Broglie wavelength } \lambda_D = \frac{2\pi\hbar}{\sqrt{2m_e kT}}$  (  $E = \frac{\hbar^2 k_D^2}{2m_e} = kT$  with  $k_D = \frac{2\pi}{\lambda_D}$  )

Typical values for QWs at 300 K:  $d_z \leq 10 \text{ nm}$

Lower limit for  $d_z$ :

- $E_{Ci} < \Delta E_C$  (bound state)
- natural barrier roughness is 1 monolayer (ML)  $\rightarrow d_z > 2 \text{ ML} \approx 1 \text{ nm}$

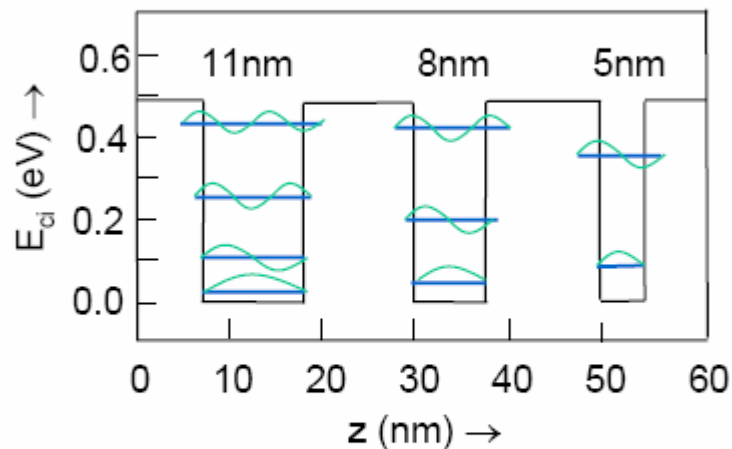
Roughness produces: - local size quantization fluctuations

- interface induced scattering

- Size quantization

### Quantum well shape

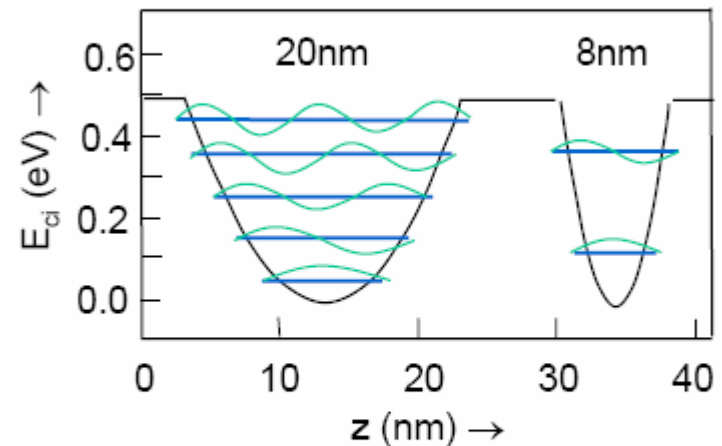
#### GaAs QWs in $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ barriers



Electron wavefunctions in a resonant cavity.

The energy eigenvalues have increasing distances.

#### Parabolic QWs in $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ barriers

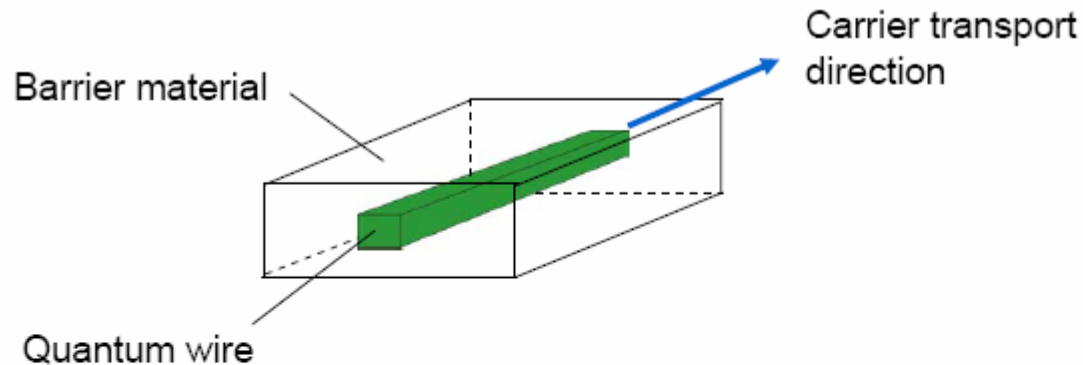


QW with graded composition.

The energy eigenvalues are equidistant

- Size quantization

### Quantum wire



Quantization of electrons and holes in two directions

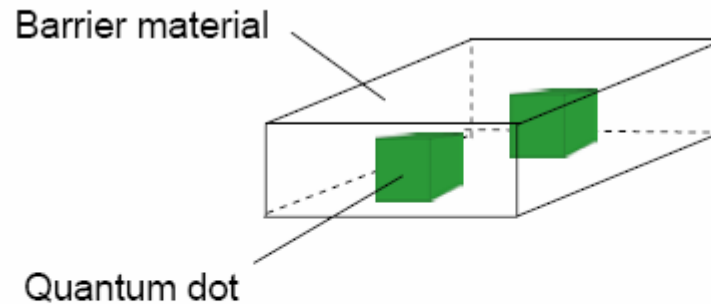
→ Dispersion relation:

$$E(\vec{k}) = E_{y,z} + \frac{\hbar^2 k_y^2}{2m_e}$$

There does not exist an elaborate preparation method for quantum wires with „bulk“ semiconductors. → Nanotubes, molecules

- Size quantization

### Quantum dots



Tree dimensional quantization

→ Atomic like system with sharp energy levels

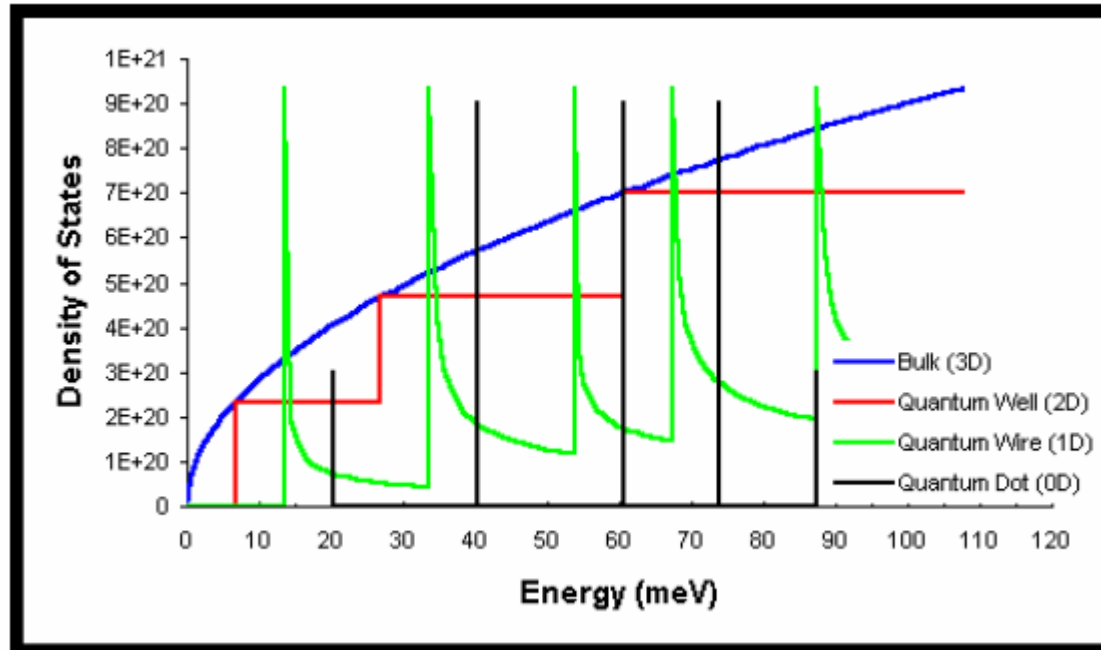
Practical realization: self-organized growth or on prestructured substrate

→ Clustering due to lattice misfit

→ Problem: size distribution

- Size quantization

### Density of states



$$\rho(E)_{3D} = \frac{1}{2\pi} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E}$$

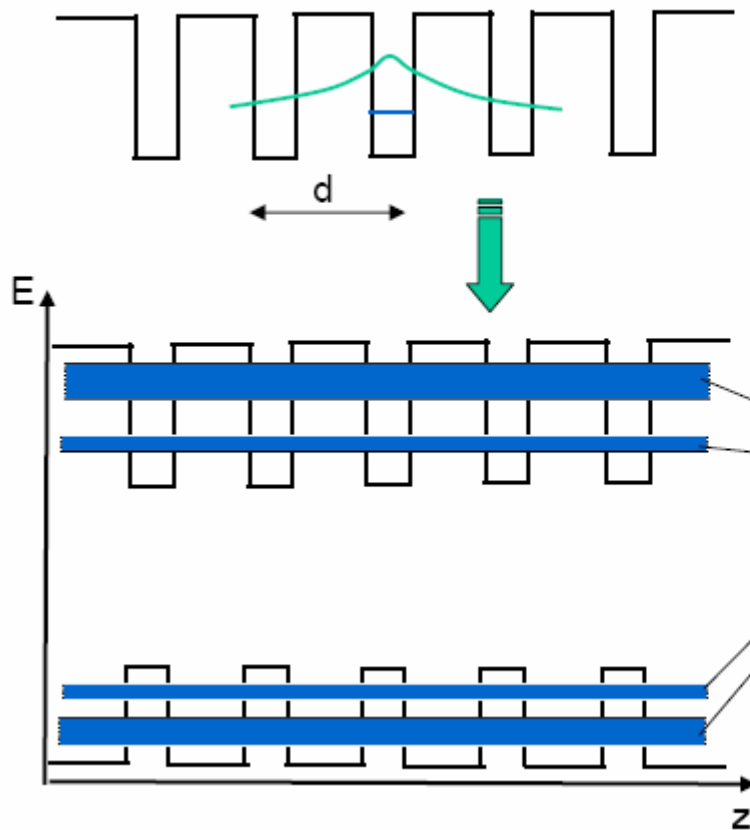
$$\rho(E)_{2D} = \frac{m}{\pi \hbar^2} \sum_i H(E - E_i)$$

$$\rho(E)_{1D} = \frac{1}{\pi} \sqrt{\frac{2m}{\hbar^2}} \sum_i \left( \frac{n_i H(E - E_i)}{\sqrt{E - E_i}} \right)$$

- Carrier transport

Periodic potentials: Superlattice (SL)

SL with N QWs



Wavefunction overlap of the N degenerate states at each energy level → minibands

Formation of minibands  
in superlattice structure

Result: electron or hole transport possible

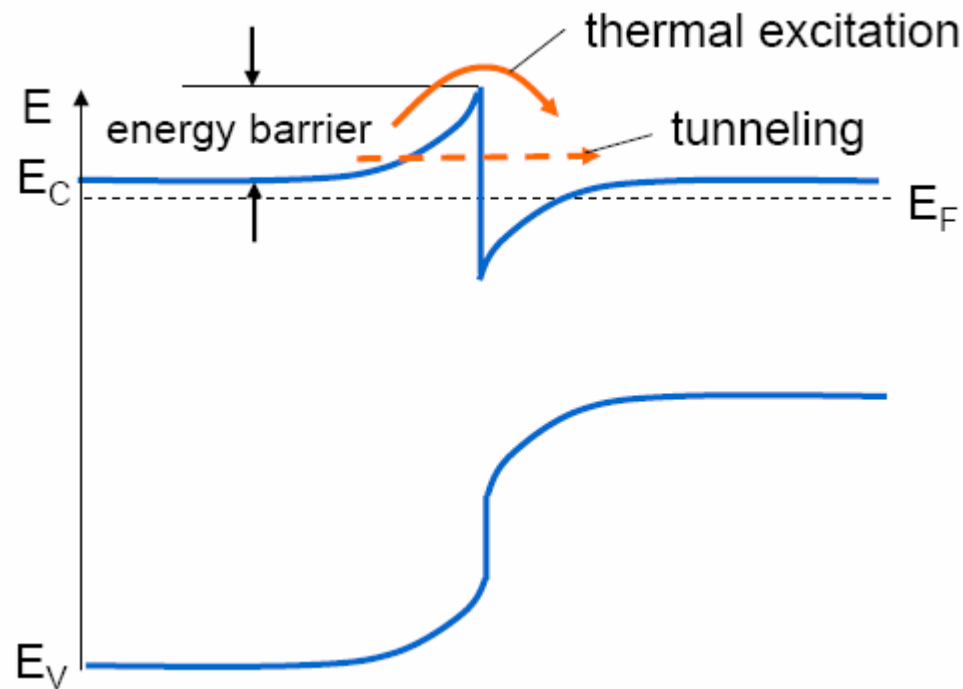


- Carrier transport

### Resistance of a heterojunction

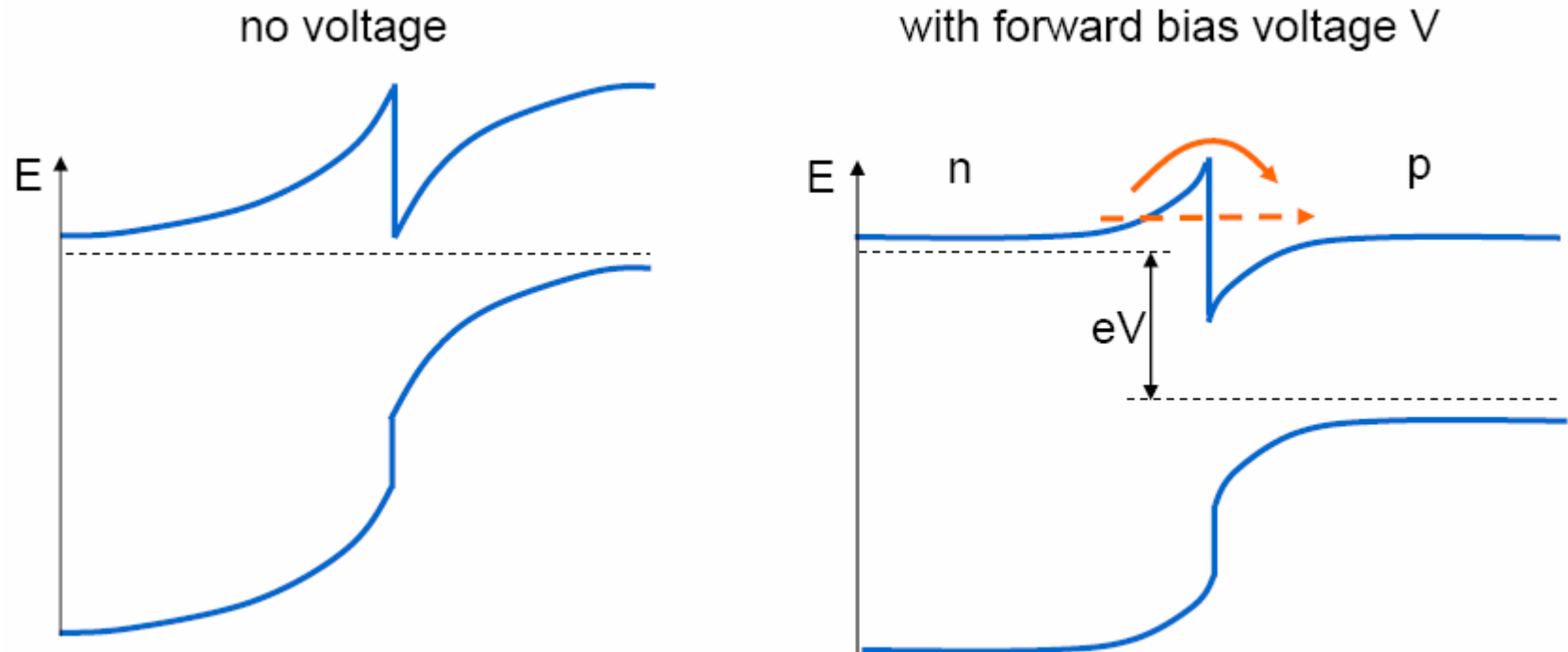
**The band edge discontinuity produces an extra resistance**

**Example:** isotype (heavily n-doped) heterojunction without voltage



- Carrier transport

### Resistance of a p-n heterojunction



The resistance can be decreased by a **graded composition**

- Spontaneous polarization

### III-nitride semiconductors

Wurtzite-phase AlN, GaN and InN show spontaneous polarization

#### Two conditions for spontaneous polarization:

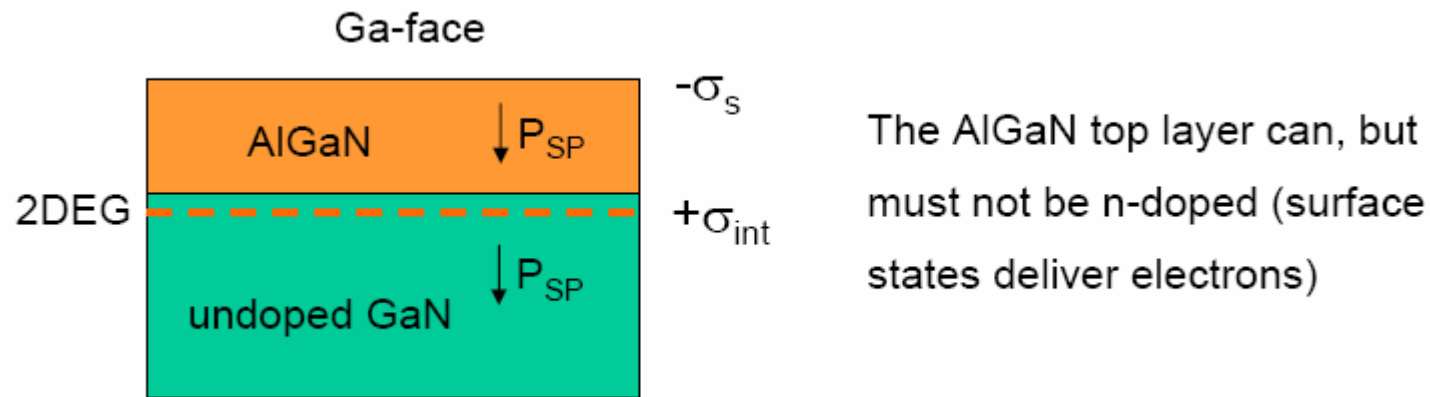
- No inversion symmetry in c-axis (metal-face or N-face)
- The  $c/a$  ratio of the unit cell is distorted from the ideal ratio  $\sqrt{\frac{8}{3}}$

#### Consequences::

- Electric dipole moment  $\rightarrow$  internal electric field  $\sim 1\text{MV/cm}$
- Polarization charges on hetero-interfaces  $\rightarrow$  2DEG possible

- Spontaneous polarization

### Hetero-interface



The III-nitrides show also a strong **piezoelectric effect**.

→ Enhancement of the two dimensional electron gas at the GaN/AlGaN interface due to stress induced polarization is possible.

The pseudomorphic heteroepitaxial growth is the source of the stress.